

# A LABORATORY ASSESSMENT OF THE SLAGGING PROPENSITY OF BLENDED COALS

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## ABSTRACT

This paper presents the results of an experimental study to assess the slagging propensity of blends of UK coals with world traded coals when burned under low NO<sub>x</sub> conditions. Coals ground to pulverised coal grade were blended in a laboratory mixer. Ash deposits were formed by passing the coals through an entrained flow reactor designed to simulate the time-temperature conditions which pulverised coal particles are subjected to in a large utility boiler. The deposits were collected on a ceramic probe at approximately 1250°C. The slagging propensity of the coal ash was assessed from a CCSEM chemical and microstructural characterisation of mounted and polished cross-sections of each deposit. The CCSEM data was used to obtain an estimate of the fraction of the deposit which would have been fluid enough for viscous flow sintering to have occurred, producing fused and bonded portions of the slags. The results indicate that the slagging propensity of a coal blend may be a non-linear function of the composition, showing both positive and negative deviations from a simple additive relationship. The findings are discussed in terms of the mineral matter transformations which occur in forming ash particles and boiler wall deposits.

## INTRODUCTION

The efficient operation of modern pulverised coal-fired boilers is dependent on fuel quality, high conversion efficiencies and a high availability of plant. The nature and quantity of mineral matter in a coal can have a profound effect on the operation and performance of the boiler. Boiler slagging not only reduces the thermal efficiency of a boiler but can give rise to other problems, such as high exit gas temperatures leading to increased fouling of superheaters and economisers. The formation of large wall deposits on water walls and superheaters can lead to blocked ash hoppers and fractured boiler tubes.

Fuel technologists have long sought reliable methods for predicting the slagging propensity of a coal ash (1). Conventional methods of assessment based on ash fusion tests, viscosity of coal ash melts and empirical indices related to the chemical composition of the ash (2) all fail to reflect the complex mineral matter decompositions and reactions which occur at the combustion temperatures. In addition, the short residence times for ash particles within the burner region (1-2 sec) frequently do not allow the larger mineral particles to reach chemical equilibrium. Advanced microstructural analysis, combined with chemical analysis of individual ash particles obtained using computer controlled scanning electron microscopy (CCSEM), has demonstrated the diverse chemical nature of ash particles and the lack of chemical homogeneity (3). Thus, to obtain reliable data, fuel technologists have developed combustion test facilities which closely simulate the conditions in large pulverised coal boilers. The results obtained with these facilities still require validation with full scale boiler trials, as recently reported by Gibb et al (4). The cost of such trials, and the need to obtain objective assessments of the slagging propensity of a coal ash provided the stimulus for the design and construction of a laboratory entrained flow reactor (EFR) at Imperial College (5) to simulate ash formation and deposition phenomena.

The EFR was designed to closely simulate the conditions which pf and ash particles experience in large utility boilers. The reactor consists of a vertical multi-zoned furnace, approximately 5m in length, with an internal diameter of 100mm. Four independently controlled furnaces heat the reactor, providing a temperature gradient from 1650°C at the top of the reactor to 1200°C or less at the bottom. A series of sample ports at approximately 1m intervals down the length of the reactor allow ash and char samples to be withdrawn from the combustion atmosphere, or for deposition probes to be inserted. Pulverised coal is introduced at the top of the furnace at a rate of 50-200g hr<sup>-1</sup>, the chosen feed rate largely depending on the ash content of the coal or blend under investigation. Gas flow rates of approximately 70 l min<sup>-1</sup> (STP), equivalent to 450 l min<sup>-1</sup> at 1650°C entrain all particles with a density of 5 g cm<sup>-3</sup> or less and a particle size of < 80µm. Under these conditions, particle residence times from top to bottom of the reactor are approximately three seconds. The reactor is shown schematically in Fig. 1, with the position of the sample ports. Gas temperatures at the top sample port are approximately 1400°C and 1250°C at the second port.

Both air-cooled metal deposition probes and uncooled ceramic probes have been used to collect ash deposits. Deposits collected at 1400°C at the first port must be collected on a ceramic probe, as it has not been possible to provide sufficient cooling of a metal probe at this port to prevent the probe from melting. The deposits are generally of a highly fused nature and give little indication of the likely slagging propensity of the coal. However, when deposits are collected at 1250°C on an uncooled ceramic probe, they range from a thin covering of lightly sintered ash particles to well-bonded and coherent deposits, the nature of the deposit depending on the proportions of the mineral matter present in the coal. These deposits most closely resemble those which form on the platten superheaters of large utility boilers and are therefore suitable for characterisation.

The ceramic probe used in this study was of simple construction, consisting of a mullite tube or coupon, 16mm OD and 12.5mm ID, and 200mm in length. The coupon is held in place over a longer (approximately 1m) mullite tube of 12mm OD. The coupon is held in place with a small amount of a high alumina cement mixed with a sodium silicate solution. The same cement was used to block the open end of the 12mm tube, thus preventing gas leakage into or out of the reactor. An aluminium holder with an "O" ring seal is used to hold the probe in position in the sample port.

#### CHARACTERISATION OF DEPOSITS

Over a 1-2hr period, the deposits varied in thickness from 2-8mm depending on the ash content and mineral matter in the coal and the feed rate. A small sample of the deposit is first removed for X-ray powder diffraction analysis to establish the crystalline phases present, while the remainder of the deposit is left undisturbed on the coupon. The deposit is then coated in a low viscosity epoxy resin, which penetrates the open porosity of the sample, but when set gives stability to even the most fragile deposits. Sections through the deposit are cut with a diamond saw, perpendicular to the surface, to give samples approximately 5mm in length. These samples are then set in resin blocks so that a cross-section through the deposit from the interface with the probe to the surface of the deposit may be examined. The samples are ground and polished to a 0.25µm diamond finish, and coated with carbon for SEM examination. At low magnification (10x) a series of backscattered images (BSI) is first obtained to give an overall view of the microstructure of the deposit. More detailed examination is then made of selected areas at higher magnifications, typically 50-100x. Quantitative chemical and image analysis data is then acquired using a Tracor Noran low element detector and Tracor Noran Voyager software. Typically, a chemical analysis is acquired using a 16x16 matrix of analysis points, giving 256 separate analyses. Quantitative EDS analyses are obtained from this data using Proza corrections. The porosity of the microstructure, which gives a strong indication of the amount of viscous flow sintering which has occurred, may be obtained from a grey scale digital image which differentiates between the ash and the resin (i.e. the filled pores) or from the fraction of analysis points reporting oxide analyses, where the criteria used for this are that analyses with  $\Sigma(\text{CaO} + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{SiO}_2) > 80\text{wt}\%$  can reasonably be assumed to be an oxide particle. The chemical and microstructural data is collected from a number of areas within each section and from samples taken at intervals along the coupon length. Typically, the number of analysis points exceeds 1000, thus giving sufficient data for reliable statistical variations to be established.

An assessment of the slagging propensity of the ash is made by a consideration of the analysis and the chemical variations shown by the ash particles and the bonding phase(s). The four main oxides which make up the ash composition are CaO,  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , and the chemical data may be analysed by normalising each ash composition to two ternary systems, i.e.  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ , and  $\text{Fe}_2\text{O}_3-\text{Al}_2\text{O}_3-\text{SiO}_2$ . Only those analyses where  $\Sigma(\text{CaO} + \text{Al}_2\text{O}_3 + \text{SiO}_2)$  or  $\Sigma(\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{SiO}_2)$  exceeds 80 wt% are taken, since the normalisation of compositions totaling less than this could lead to substantial errors. The data obtained may then be plotted on a ternary diagram, see for example Fig.2. Each plot shows not only the range of chemical compositions obtained by analysis, and thus the degree of chemical inhomogeneity in the sample, but also indicates the degree of interaction between the decomposed mineral residues, i.e. the clays (kaolinite and illites), pyrite, calcite, quartz etc.

The quartz and decomposed clays can be considered as relatively refractory materials at the combustion temperatures. Indeed, coals which contain only these minerals give few problems with regard to boiler slagging. Any ash which forms on the boiler walls is little more than a friable dust with no mechanical strength. Slagging problems arise if the mineral matter contains additional minerals such as pyrite ( $\text{FeS}_2$ ), calcite ( $\text{CaCO}_3$ ), dolomite ( $\text{Ca.Mg}(\text{CO}_3)_2$ ), siderite ( $\text{FeCO}_3$ ), and ankerite ( $\text{Ca.Fe}(\text{CO}_3)_2$ ). Each of these minerals decomposes to give the respective oxide, which acts as a strong fluxing agent for the aluminosilicate phases, lowering both the liquidus temperature and the viscosity of the melt. On a mole for mole basis, FeO is a more powerful fluxing agent than CaO, since the  $\text{Fe}^{2+}$  ion is smaller in size than the  $\text{Ca}^{2+}$  ion, enabling the aluminosilicate anions to move over each other more readily. Aluminosilicate ash particles which

have been fluxed with either FeO or CaO, or both, have the potential to form sticky ash particles which will not only adhere to a surface (water wall or deposit) but will bond together the more refractory ash particles. Exactly how much FeO or CaO is required to form a sticky ash particle remains open to debate, but lower limits of 5-10 wt% would be considered a reasonable estimate. At higher concentrations of FeO or CaO, a reverse of the fluxing role of these oxides is observed. In the case of FeO, a solubility limit is reached, and the excess iron oxide is precipitated from solution in the form of iron oxide dendrites (magnetite or haematite). Ash particles with more than 50 wt% Fe<sub>2</sub>O<sub>3</sub> are therefore more than likely to be mainly solid crystalline iron oxides and thus of relatively low slagging propensity. CaO, which itself is refractory oxide, lowers the liquidus temperature and the viscosity of aluminosilicates, with a maximum effect on coal ash compositions at 25-30 wt% of added CaO. Further increases lead to increasing liquidus temperatures and a reduction in the amount of liquid phase present (6). Ash particles with 40% or more of CaO may similarly be considered as non-slagging particles, at least in the early stages of the formation of deposits. An EFR slagging index has therefore been established by determining the fraction of ash particles which contain 10-50 wt% of Fe<sub>2</sub>O<sub>3</sub>, or 5-40 wt% CaO.

#### COAL BLENDS

Two UK power station coals (coals 1 and 2) were chosen for blending with a Colombian coal (coal 3), two US coals (coals 4 and 5) and a South African coal (coal 6). The ash content and ash composition for each of these coals is shown in Table 1. Coals were each ground separately to pf grade, i.e. 70% less than 75µm. The coals were then blended in a laboratory mixer in batches of 1-2 kg. Coal were dried at 110°C for several hours before feeding to the EFR for the ash deposition studies. Failure to dry the coals sufficiently resulted in uneven flow rates of pf from vibratory hopper, which in turn caused blockages of the pf in the water-cooled injection probe at the top of the reactor.

#### RESULTS AND DISCUSSION

The results of blending coal 1 (UK) with coal 3 (Colombian) are shown in Fig. 3. In order to assess the sensitivity of the EFR slagging index, the CCSEM data has been analysed here using three sets of compositional limits in determining the fraction of ash particles which would be deemed to be of a fluxed nature and a low viscosity. The conditions chosen were as shown below.

Conditions	CaO (wt%)	Fe <sub>2</sub> O <sub>3</sub> (wt%)
A	5-40	10-50
B	5-45	5-55
C	10-35	15-45

In all three cases, the variations in slagging propensity with the addition of coal 3 are similar, with initially an increase in slagging propensity which shows a significant positive deviation from a simple law of mixtures. Conditions B, which provide the widest compositional limits give the highest values for the EFR slagging index, while conditions C, with the narrowest range give the lowest values. Conditions C also show the smallest variations and thus the least sensitivity to compositional changes and related microstructural changes. Fig. 4 shows the variations in slagging indices obtained on blending the two UK coals with the overseas coals. In each case, major deviations were observed from a simple linear relationship between the slagging index and the blend composition. The data shown in Fig. 4 was obtained using the compositional limits A in each case. These conditions were chosen as giving the optimum measure of the compositional variations in each deposit. In each case, the addition of the overseas coal initially gave a marked increase in the slagging propensity, with a maximum value in the range 25-50 wt% of added overseas coal. Above 50 wt% of the added coal, the slagging propensity decreased, in two cases with negative deviations from a linear relationship.

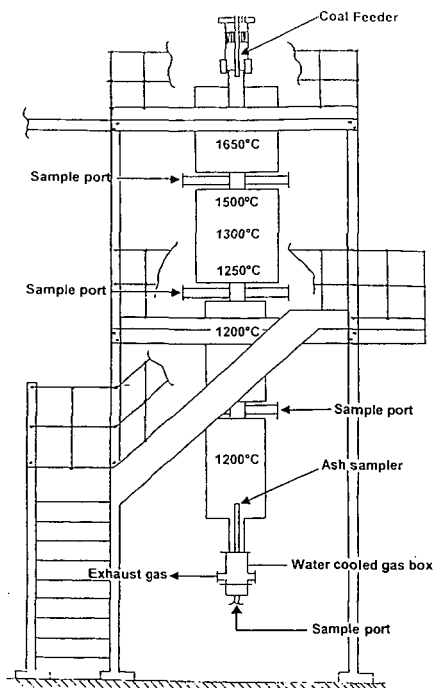
In a blended pf, there are basically two types of mineral matter. Most of the adventitious mineral matter present in the original coal is liberated as discrete mineral particles during the grinding process, while the finely distributed inherent minerals remain within the coal particles. It is generally assumed that the discrete mineral particles exhibit little interaction during the ash formation processes, reacting only with other ash particles on deposition. Inherent minerals interact and coalesce during the combustion of the char and are responsible for the wide range of aluminosilicate compositions observed for ash particles. Synergistic effects between ash particles suggests that complex interactions between particles must occur, and these are most likely to take place following deposition to form the slag.

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Table 1 Coal ash compositions (wt%) and ash contents

Coals	1	2	3	4	5	6
wt% ash	9.8	16.0	8.6	8.7	8.5	14.8
SiO <sub>2</sub>	41.9	56.0	63.5	50.0	48.2	40.7
Al <sub>2</sub> O <sub>3</sub>	24.3	26.4	19.9	25.6	21.1	32.7
Fe <sub>2</sub> O <sub>3</sub>	20.9	6.5	8.5	14.6	16.5	2.4
CaO	7.1	1.9	2.6	4.5	4.4	9.3
MgO	3.3	1.7	1.7	1.0	1.0	2.5
Na <sub>2</sub> O	0.1	1.5	0.6	0.8	1.4	0.4
K <sub>2</sub> O	1.0	4.0	2.2	2.0	2.2	0.7
P <sub>2</sub> O <sub>5</sub>	0.2	0.1	0.2	0.4	0.3	1.4
TiO <sub>2</sub>	1.0	1.0	0.9	1.2	1.2	1.7
MnO	0.2	-	0.1	<0.1	-	-



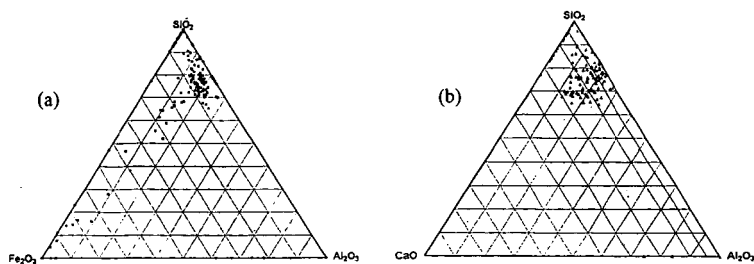


Fig. 2. Chemical inhomogeneity of slags as shown by EDS point analysis of polished cross-sections. Each composition has been normalised to (a)  $\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{SiO}_2$ , and (b)  $\text{CaO} + \text{Al}_2\text{O}_3 + \text{SiO}_2$  for plotting. Shaded areas are compositions deemed to be slugging.

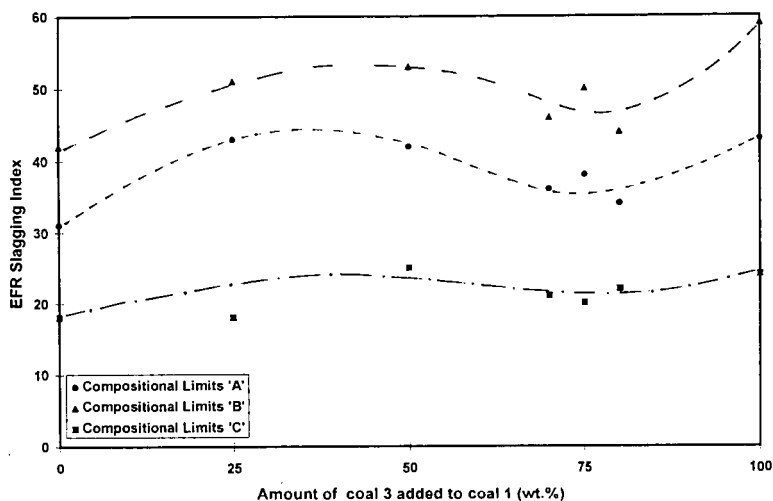


Fig. 3. Variation in EFR slagging index obtained with blends of coal 1(UK) with coal 3 (Colombian). Compositional limits A,B and C represent different concentrations of  $\text{Fe}_2\text{O}_3$  and CaO in fluxed ash particles, see text for full details.

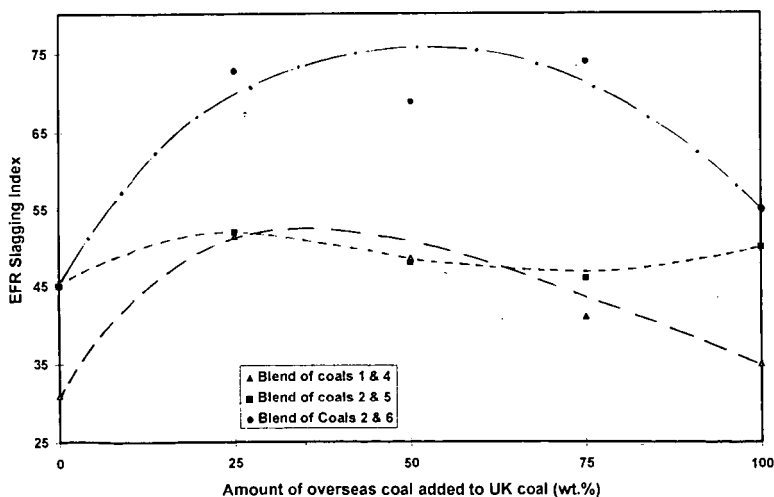


Fig. 4. EFR slagging indices for blends of UK coals 1 and 2, with overseas coals 4, 5 and 6.